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AN APPROACH TO THE KINETICS OF WATER DESORPTION FROM A-ZEOLITES. PART I. ISOTHERMAL AND NON-ISOTHERMAL DESORPTION *

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ABSTRACT

Desorption of water from zeolites: NaA, LiA, KA, CdA, ZnA, MgA and CaA were examined. Isothermal and non-isothermal kinetic analyses were carried out. It was found that the process of desorption can be presented as a first-order reaction. Due to the existence of several water–zeolite complexes, neither isothermal nor non-isothermal kinetic methods may be applied directly.

INTRODUCTION

Desorption from an ideal, energetically homogeneous surface is usually presented by the well-known Polanyi–Wigner equation [1], i.e.

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = k\theta^n \tag{1}$$

where θ is the degree of coverage, k is the rate constant, and n is the reaction order.

Real systems are usually heterogeneous and can only be presented by this equation as a rough approximation [2]. There are several methods of representing desorption kinetics from a heterogeneous surface. The equation which is most commonly used which relates kinetic parameters, activation energy and pre-exponential factor, to the degree of coverage can be expressed in the form

$$-\frac{\mathrm{d}\theta}{\mathrm{d}t} = A(\theta)\exp\left[-\frac{E(\theta)}{RT}\right]\theta^n \tag{2}$$

However, application of eqn. (2) presents many problems. The most im-

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portant one is in connection with the pre-exponential factor. According to the transition-state theory, the pre-exponential factor is equal to the constant kT/h (10^{13} s^{-1}) and it should be valid for eqn. (1) [3]. In reality, significantly larger [4] or smaller [5] pre-exponential factors were obtained. Besides, eqn. (2), cannot be applied to processes in which readsorption or formation of several complexes takes place.

The method of isothermal kinetics, can only give proper results for homogeneous surfaces [eqn. (1)]. In other cases, using eqn. (2), or similar equations, it is impossible to obtain any results or they are insufficient.

On the other hand, the methods of non-isothermal kinetics (thermokinetics) which have been developed in recent years are much more suitable.

During desorption from a homogeneous surface under non-isothermal conditions, one peak appears. The shape of the thermodesorption peak depends on the heating rate and kinetic parameters. A few, general thermokinetic methods have been established [6–8].

Thermodesorption peaks from a heterogeneous surface are much more complicated. Their shape and position depend on several factors: type of heterogeneity, possible reactions on the surface, heating rate, reaction order and the initial degree of coverage.

Thermodesorption from a heterogeneous surface can, in principle, be described by eqn. (2). However, there are difficulties in the application of this equation because it is necessary to determine two functions, $A(\theta)$ and $E(\theta)$, on the basis of only one equation. The method suggested by Yakerson et al. [2] is applicable if the system is such that the change of activation energy with θ is an elementary mathematical function. However, $E(\theta)$ is usually a complex function [10]. (Results are confirmed in many cases by thermodynamic data.) The formation of adsorption complexes on the surface also leads to a complex thermodesorption peak [11]. In this case, instead of eqn. (2), an equation containing several rate constants is necessary. Its shape will depend on the mechanism of the process [12].

All investigations by various methods (IR [13], NMR [14,15]) indicate that water on zeolites has a very complex structure. So, very complex kinetics from several centers and different distributions can be expected. This is probably the reason for the lack of data in the literature concerning the thermokinetics of water from synthetic zeolites [16–19]. Cruceanu and Biro [17] applied the method of Horowitz–Metzger to the dehydration of various commercial zeolites. Dyer and Howes [18] examined the desorption of water from hydrothermally damaged zeolite 4A. Kelly et al. [19] examined dehydration from Y and L-zeolites. It is difficult to compare the results obtained not only because of the possibility of the existence of complex reactions but also because of the application of various thermokinetic methods.

EXPERIMENTAL

The basic materials were Union Carbide 4A zeolites in powder form. The exchanged forms of LiA, MgA, CdA and ZnA were prepared by standard ion-exchange procedures [20]. The samples were prepared by the sorption of water on zeolite dehydrated in vacuum (10^{-3} torr) for 3 h at 400°C. DuPont 990 and Perkin-Elmer DSC-1B thermal analysers were used to follow the desorption kinetics. Differential scanning calorimetry (DSC), effluent gas analysis (EGA) and thermogravimetry (TG and DTG) were applied. Investigations were carried out in a wide range of heating rates (0.5–64° min^{-1}) in a dry nitrogen flow of 15 ml min^{-1}.

Calculations of the kinetic parameters were performed on PDP-11 and Hewlett-Packard 9931 computers. Appropriate programs were set up for the polynomial method [21] and methods [6–8] for determining kinetic parameters.

RESULTS AND DISCUSSION

Isothermal water desorption was carried out in the temperature interval 350–450°C. Typical isothermal results are shown in Fig. 1 for the system NaA–H_2O.

As may be seen from Fig. 1(a), desorption is a first-order reaction in the temperature range examined. The logarithm of the rate constant [Fig. 1(b)] is

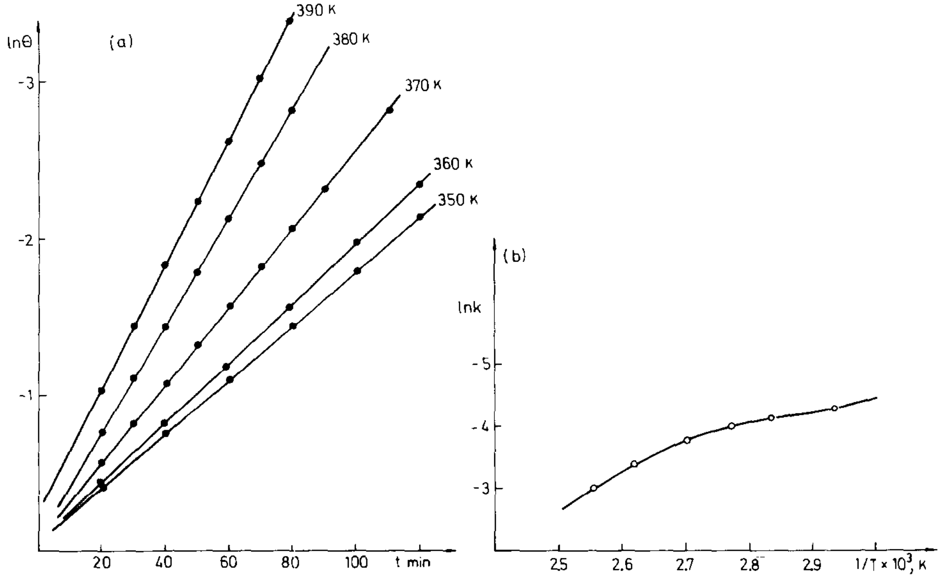

Fig. 1. Isothermal water desorption from NaA zeolite. (a), Kinetic desorption curves at various temperatures; (b), Arrhenius plot of water desorption from NaA zeolite.

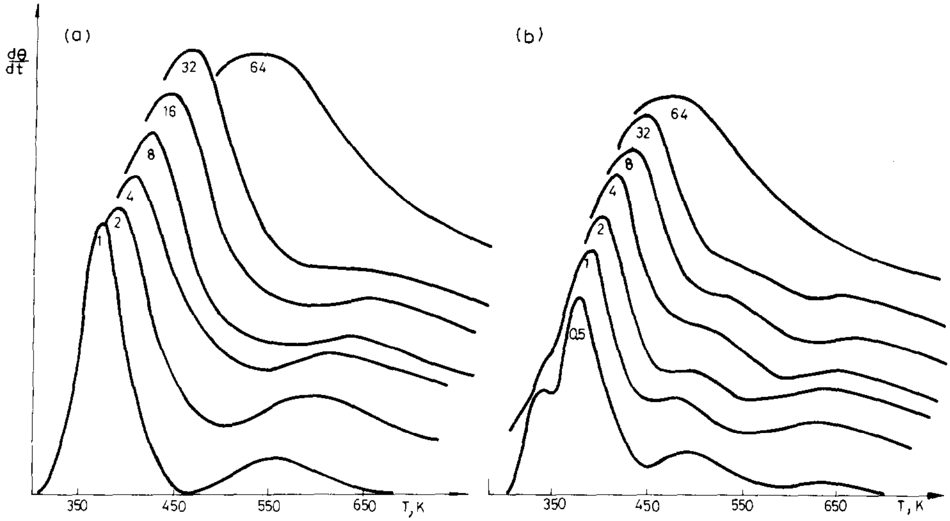

Fig. 2. Water desorption at various heating rates (0.5–64° min^{-1}). (a), EGA of water from LiA; (b), EGA of water from MgA.

not a linear function of $1/T$, therefore it is not possible to determine the activation energy or the pre-exponential factor. Similar results were obtained for water desorption from LiA, KA, MgA, CaA, CdA and ZnA zeolites. Non-isothermal desorption of water from zeolites is characterized by several peaks in DSC, DTG and EGA or saddles in TG curves. The position and number of peaks depend on the type of zeolite, counterions [22–27], heating rate and degree of coverage. Zeolites with monovalent counterions, having the maximum degree of coverage and using an average heating rate (4–10° min^{-1}), have three peaks. Zeolites with bivalent cations exhibit four [26]. An increase in the heating rate leads to peak overlap. Figure 2 shows typical desorption for different heating rates (initial degree of coverage, $\theta = 1$). For low heating rates,three or four peaks exist, while at 64° min^{-1} there is only one very broad peak. Full peak resolution does not occur. even at 0.5° min^{-1}. Changes of the initial degree of coverage change the position and number of peaks. Figure 3 shows the results of effluent gas analysis obtained at a heating rate of 1° min^{-1}. When the initial degree of coverage is changed from $\theta = 1$ to $\theta = 0.1$, only the high-temperature peak does not depend on temperature. The results suggest very complex zeolite–water interaction. Direct application of integral and differential methods of non-isothermal kinetics [7–9] to such complex systems is not possible. Instead of linear dependences which are the basis for kinetic parameters determination, complex non-linearizable functions were obtained.

The appearance of several peaks complicates the application of methods in which the kinetic parameters are determined by the shift of the peak maximum for different heating rates. The best approximation was obtained

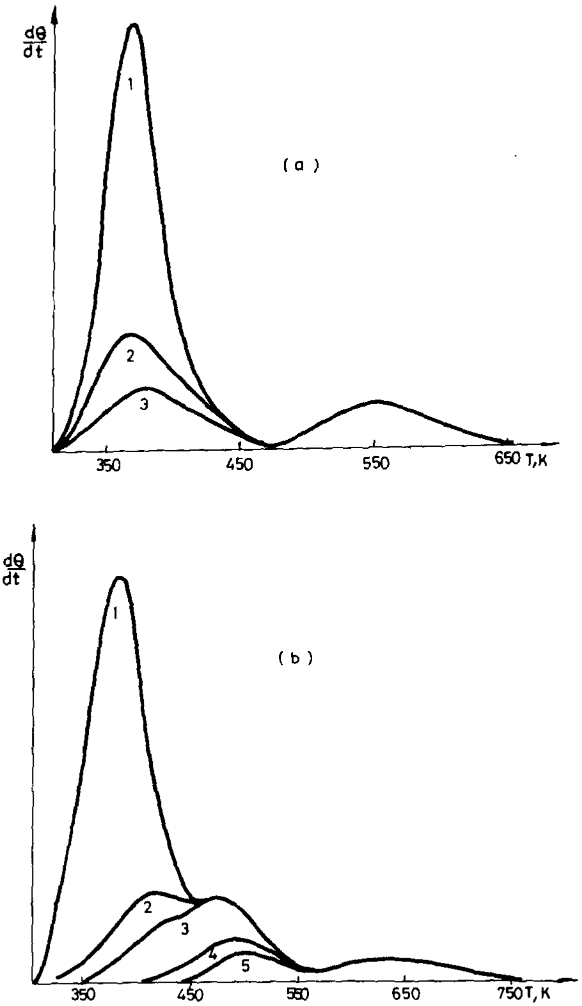

Fig. 3. Water thermodesorption at various degrees of coverage. (a), EGA of water from LiA; (b), EGA of water from MgA.

using the method of Redheads [6] applied to zeolites with monovalent cations and with a degree of coverage of less than $\theta = 1$. The results are shown in Fig. 4. From these results it was found that the middle desorption peak corresponds to the first-order reaction with an activation energy of 37–46 kJ mole^{-1}. The activation energy of the low and high-temperature peaks could not be determined due to peak overlapping and broadening.

The method of Bauer et al. [10] was applied to complex thermograms but it did not give satisfactory results in the case of zeolites. The appropriate functions are not linear and cannot be used.

An attempt was made to determine the kinetic parameters by using the polynomial method [21]. According to this method, the activation energy

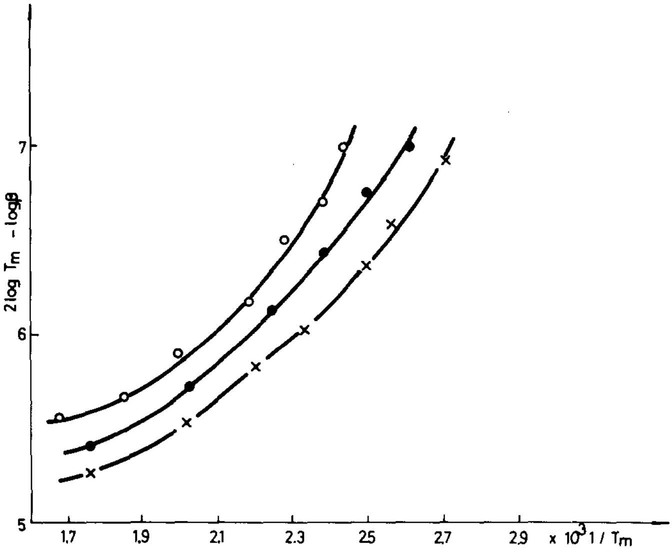

Fig. 4. Application of the Redhead method [6] to water desorption from X, LiA; ●, NaA; ○, KA zeolites

changes with the degree of coverage as an *n*th order polynomial, while the pre-exponential factor does not depend on the degree of coverage. The polynomial coefficients and pre-exponential factor are determined by the least-squares method from experimental curves. The kinetics are described by eqn. (2) in which $A = \text{const}$.

Polynomials from the first to eighth order were calculated. The results for the best fitting polynomials (fifth and sixth order) are presented in Fig. 5(a) and 5(b). The calculated thermodesorption curves differ significantly from the experimental curves.

A last attempt was made to calculate $E(\theta)$ from eqn. (2) using different values of the pre-exponential factor. For different experimental values of $d\theta/dt$ (DTG), the corresponding $E(\theta)$ was computed. Figure 6 shows the results obtained for a first-order reaction when the pre-exponential factor is changed from 10^2 to 10^{15} s^{-1}. As can be seen, $E(\theta)$ depends on the value of the pre-exponential factor. It is only when the pre-exponential factor is of the order of 10^5 s^{-1} and the reaction is first-order that the calculated function $E(\theta)$ slightly resembles the experimental function (differential heat of adsorption) [28]. This is much more evident when a comparison is made between the computer plot of dQ/dt vs. temperature and the corresponding experimental DSC curve, Fig. 7, (The computer plot, dQ/dt, was calculated from the $E(\theta)$ found from Fig. 6.) It is evident that not only the shape, but even the position of the peaks depend on the pre-exponential factor. The best resemblance was achieved for the factor 10^5 s^{-1}. This approach cannot lead to an agreement between experimental and calculated curves which is

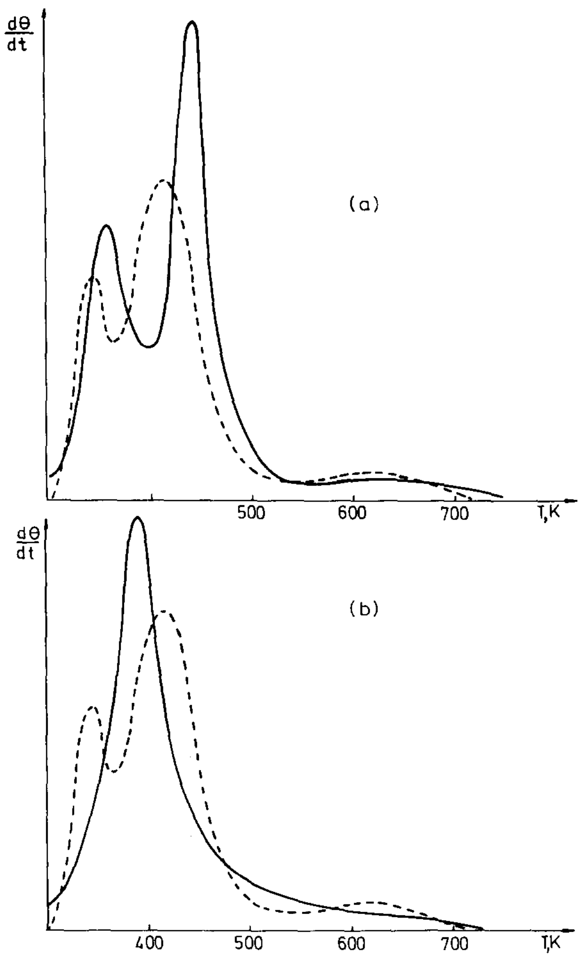

Fig. 5. Application of the polynomial method to water desorption from NaA zeolites. - - - - - -, Experimental curves obtained by DTG for the heating rate 10° $\min^{-1}$ and $\theta = 1.36$; ————, calculated curve. (a), 6th-order polynomial; (b), 5th-order polynomial.

better than 25%. [An attempt to improve the results by using $n = 2$ in eqn. (2) leads to an even worse agreement.]

On the basis of the results presented, it is evident that kinetic methods, both isothermal and non-isothermal, cannot be applied to zeolite dehydration: even if the equations are used in the most general forms, the activation energy and pre-exponential factor depend on the degree of coverage. This result can be accepted only if several DSC peaks correspond to the thermodesorption from several, more or less independent, water–zeolite complexes. Some X-ray [29] and NMR [14] experiments fully support this hypothesis.

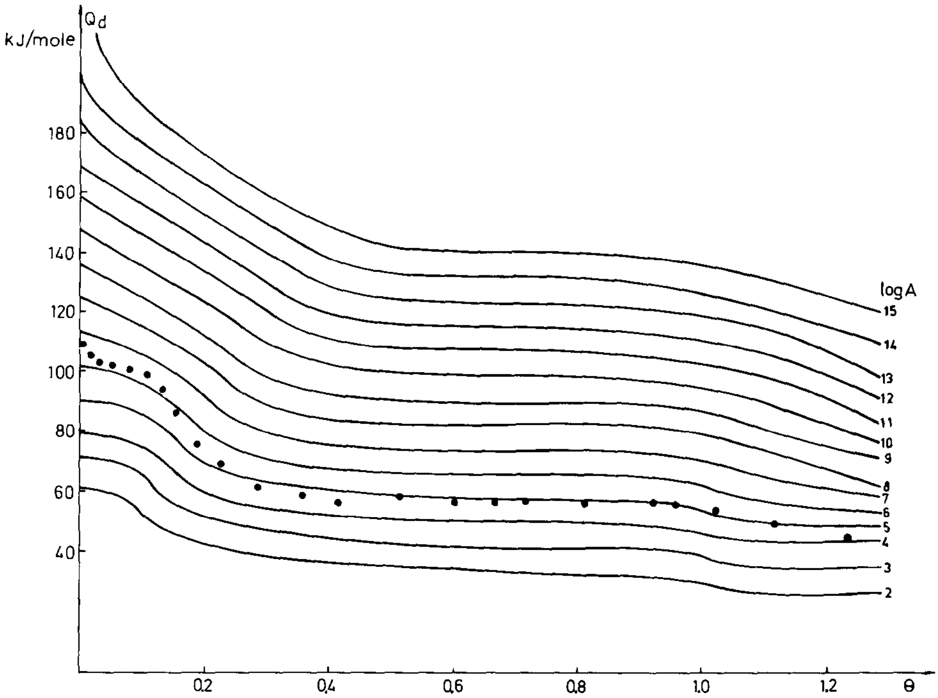

Fig. 6. Computer plot of the activation energy as a function of the degree of coverage for various pre-exponential factors, in the system NaA–H_2O. ●, Experimental differential heat of adsorption [28].

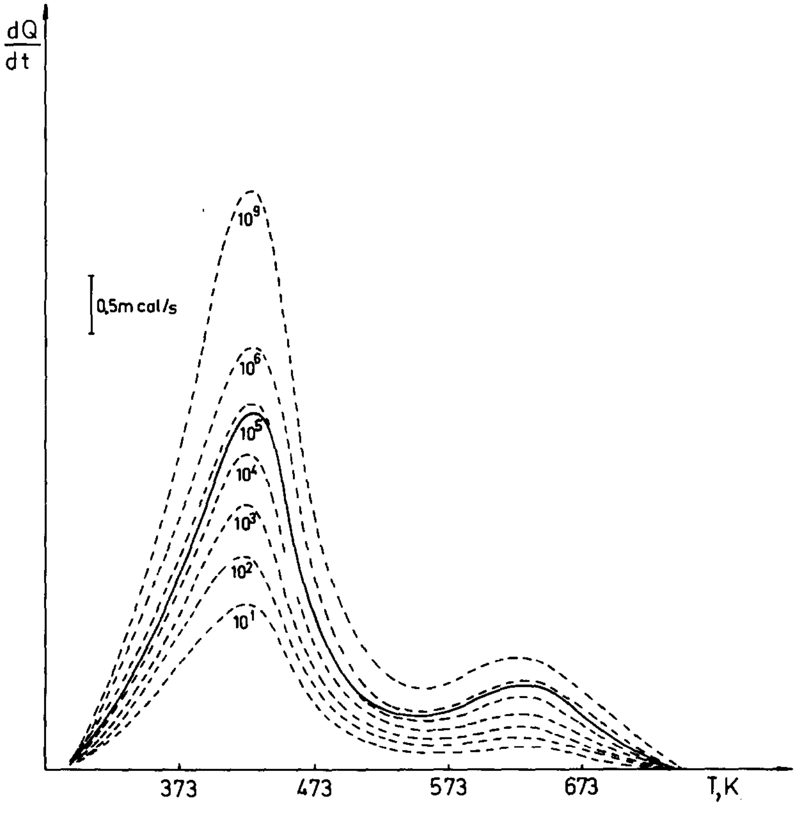

Fig. 7. - - - - - -, Computer plots of calculated DSC curves with various pre-exponential factors for the system NaA–H_2O at a heating rate of 10° min^{-1} and $\theta = 1$; ———, experimental DSC curve.

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